A

Thesis

on

PHOTODEGRADATION OF AMMONIA USING MIL-125 AS A POTENTIAL PHOTOCATALYST

Submitted by

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Under the guidance of

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Certificate

This is to certify that this Thesis entitled "***Photodegradation of ammonia using MIL-125 as a potential photocatalyst***" submitted by Nikhil Rahul Dhabarde, Roll number 214CH1098, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of Master of Technology in Department of Chemical Engineering. Neither this thesis nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Date:

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Dedicated

To my beloved parents

<u>Rahul Dhabarde</u>

&

<u>Veena Dhabarde</u>

Declaration of Originality

I, Nikhil Rahul Dhabarde, Roll Number *214CH1098* hereby declare that this thesis entitled *Photodegradation of ammonia using MIL-125 as a potential photocatalyst* presents my original work carried out as a post graduate (M.Tech.) student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the thesis. Works of other authors cited in this thesis have been duly acknowledged under the sections "References". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 25, 2016

NIT Rourkela Nikhil Rahul Dhabarde

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ABSTRACT

Metal Organic frameworks have shown promises in adsorption, gas separation, gas storage, catalysis, drug delivery and sensing. MOFs have shown potential as heterogenous catalysts as well. Their high surface area, tunable porosity, diversity in metal and functional groups, pore volume and active metal sites make them attractive proposition to be used as catalysts. Heterogeneous photocatalysis is one of the most attractive technologies for the degradation of organic substances present in wastewater. Literature reports conclude MIL-125(Titanium based MOF) has a great potential in photocatalysis. In our present area of research, we report a novel rapid synthesis procedure of MIL-125. Detailed characterizations were carried out using various techniques like SEM, PXRD, TGA, BET surface area analysis, FTIR and UV reflectance study. A detailed aqueous phase stability study followed which showed its stability under various pH conditions. The specific surface area of approx. 371 m^2/g showed the porous nature of the synthesized samples whereas the corresponding band gap energy value was found to be 3.18 eV. Ammonia degradation study was carried out using MIL-125 and the results were found to be consistent. The final degradation of ammonia was found to be approx. 70% and the experimental data were best fit pseudo first order kinetic model where the rate constant was found to be 0.03189. Two more variants of MIL-125 were synthesized viz. Fe doped and MIL-125 Solvothermal. Both the products were found to be porous with an experimental measured surface areas of 246 m^2/g and 240 m^2/g, respectively. The corresponding band gap energy were 3.4 eV and 3.2 eV. These preliminary evaluation shows the potential of both the samples and further investigation are necessary to find their effectiveness.

Keywords: *Metal Organic Frameworks (MOFs), MIL-125, phototcatalysis, microwave synthesis, ammonia degradation*

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Nomenclature

BDC	-	Benzene dicarboxylic acid
BET	-	Brunauer, Emmett and Teller
DMF	-	Dimethyl Formamide
DSC	-	Differential Scanning Calorimetry
EDX	-	Energy Dispersive X-Ray Spectroscopy
EM	-	Electromagnetic
EPA	-	Environment Pollution Act
FTIR	-	Fourier Transform Infrared
HPMV	-	High Pressure Mercury Vapor
LECA	-	Light Expanded Clay Aggregate
MIL	-	Matérial Institut Lavoisier
MOF	-	Metal Organic Framework
MW	-	Microwave
PXRD	-	Powder X-Ray Diffraction
RhB	-	Rhodamine B
SEM	-	Scanning Electron Microscope
STP	-	Standard Temperature Pressure
TGA	-	Thermogravimetric Analysis
UV-*vis*	-	Ultraviolet Visible

I. INTRODUCTION

The Metal Organic frameworks are crystalline hybrid materials assembled from inorganic and organic building blocks. It is based on the self-build of cationic systems acting as nodes with polytropic organic ligands acting as linkers [1].

1.1 PRELUDE

The rapidly expanding field of MOF is evinced from the exponential growth with respect to the various scientific publications delineated and the accompanying contemporary materials pioneered prior to last decade. While the evolving studies in the 1990s related with MOFs were predominantly confined to the chemistry discipline, nowadays, research activities on MOF type materials are extremely dynamic and highly cross-disciplinary. In principle, these same MOFs could also be used for catalysis due to their shape and size selectivity and their attainable bulk volume. Additionally, mass transport in the pores is not restrained because of their very porous framework [2].

Background of research

Metal Organic Frameworks or MOFs are essentially known for their flexibility in structural architecture. Appropriate selection of inorganic metal atoms/ions and organic ligands lead to a range of probabilities in topology and functionalities within MOFs. This very fact has been exploited by researchers across the globe in great detail with a reported finding of more than 2000 different MOF structures. Remarkable specific surface area (ca. 100-5500 m^2 g^{-1}) and pore volume (0.5-3.5 ml g^{-1}), uniform pore size distribution, tunable or tailor-made matrices, product purity, variety in functionality and aperture size/shape are few of the key features of this class of materials. The prominent features of MOFs have attracted wide attention within the research fraternity ever since its genesis and found applications in areas ranging from adsorptive gas purification /separation, energy storage, catalysis, drug delivery, sensors, etc [1].

MOFs can therefore be adapted for a vast variety of optical applications, including luminescent pH sensors, tunable light emitters and photocatalysis. The pollution of surface and ground

waters caused by waste waters with a high load of nitrogen compounds like urea, amines, NH_4^+ / NH_3, NO_2^- and NO_3^- is becoming more and more problematic. In natural waters they mainly cause eutrophication. NH_4^+ / NH_3, urea and amines also increase the biological oxygen demand and NH_4^+ / NH_3 is toxic to fish [4]. In order to solve the environmental problem, physical and chemical processes have been examined. Several methods have been proposed for ammonia removal from wastewater such as biological process, stripping, ion exchange, breakpoint chlorination, electrochemical process and photocatalysis [5]. Among these techniques, heterogeneous photocatalysis is one of the most attractive technologies for the degradation of organic substances in wastewaters. MOFs have potential as heterogeneous catalysts. Their high surface area, tunable porosity, diversity in metal and functional groups make them especially attractive for use as catalysts [3].

The photocatalytic method for degradation of ammonia is interesting because of its preferences characteristics such as minimal generation of secondary waste, simple operation, remote control, inexpensiveness and high efficiency [5]. The most effective and commercially available photocatalytic material is semiconducting titanium dioxide (TiO_2). We are going to synthesize a titanium based MOF which can be much more effective than TiO_2 itself. A systematic study of the photocatalytic degradation of different kinds of nitrogen compounds with respect to the mechanisms of their degradation will be necessary.

1.2 RESEARCH OBJECTIVES

The prime objectives of the research can be embodied as follows:

a) Rapid synthesis of Titanium based MIL-125 metal organic framework (MOF) using microwave route.
b) Optimisation of the synthesis methodology and characterization of products formed.
c) Study of aqueous phase stability of MIL-125 on its structural and functional integrity for its suitability in photocatalytic application.
d) Comprehensive photodegradation study of ammonia as an inorganic substrate using synthesised photo catalyst.

1.3 THESIS SUMMARY

This thesis has been arranged in the chronological order of 5 chapters. **Chapter 1** i.e. Introduction outlines history of MOFs, background research and motivation, ammonia pollution and photocatalysis application. **Chapter 2**, Literature review, gives in depth view of MOF synthesis, photocatalytic nature of MOF, Titanium Dioxide as precursor of MIL-125. **Chapter 3** is Experimental Works explains the miscellaneous materials and resources utilized and the experimental protocols followed. **Chapter 4**, Results and Discussions, details about the various findings we came across while carrying out various procedure of synthesis authenticated by characterization and the experiments with appropriate references. **Chapter 5**, Conclusion and Future scope, concludes the research summary and emphasizes possible further expansion of the present work.

II. LITERATURE REVIEW

It is noteworthy to mention here that a careful review of the literature reveals more than 2,000 different MOF structures being synthesized and characterized.

2.1 TYPES OF SYNTHESIS

Various synthesis methodologies have been developed through reticular synthesis. Some of these techniques that have been employed for synthesis of MOFs are,namely, solvo-thermal, ultrasonic enhanced synthesis, electrochemical synthesis, mechanochemical synthesis, atmospheric synthesis and microwave synthesis. Most of these techniques can be clearly understood as their namesakes. But, solvo-thermal and microwave synthesis are among the highly productive and applied methods. Solvo-thermal being the traditional, while latter is in modern category.

Solvo-thermal/Hydrothermal Synthesis

Conventionally MOF synthesis was first practiced using solvo-thermal technique in which no side reaction takes place and temperature of the reaction was the paramount factor deciding the quality and yield of product. It can be described as a method of synthesis of single crystals and different chemical compounds that depends on the solubility of minerals in solvent under pressure over 1 atm. The crystal growth is achieved in an apparatus consisting of a steel pressure vessel called autoclave. These vessels are made of thick-walled steel materials which must withstand high temperatures and pressures for long period of time. As different solutions are used for synthesis, to prevent corrosion of the internal cavity of the autoclave, protective inserts are generally used. In this research only Teflon liners are used. The samples are placed first in the Teflon bags, then these bags are kept in Teflon liner and closed with a cap on the top, then this cup is placed into the autoclave. The autoclave is closed tightly. Solvothermal reactions are carried out in closed vessels under autogenous pressure above the boiling point of the solvent. In conventional solvo-thermal process, crystal grows and nucleates near the walls of the reaction vessel or on the dust particles present in the solution mixture resulting in slow growth [6]. Later on, non solvo-thermal techniques of synthesis came into existence, in which the reaction takes place at ambient pressure and temperature as exemplified by Hoskins

and Robson. Further development in field of crystallization has led into new advent of synthesis technologies like high throughput methods, in-situ and ex-situ crystallization of MOF

Microwave synthesis

Microwaves are the electromagnetic waves with vacuum wavelength ranging between 0.1 to 100cm or corresponding frequencies between 0.3 to 300 GHz. Microwave assisted synthesis relies on the interaction of electromagnetic waves with mobile electric charges. These can be polar solvent molecules/ions in a solution or electrons/ions in a solid. In the solid, an electric current is formed and heating is due to electric resistance of the solid. In solution, polar molecules try to align themselves in an electromagnetic field and in an oscillating field so that the molecules change their orientations permanently. Thus, applying the appropriate frequency, collision between the molecules will take place, which leads to an increase in kinetic energy, i.e. temperature of the system. With microwave heating, the energy can be applied directly to the sample rather than conductively, via the vessel. Due to the direct interaction of the radiation with the solution/reactants, MW-assisted heating presents a very energy efficient method of heating. Thus, high heating rates and homogeneous heating throughout the sample is possible. Here, crystals are formed throughout the bulk solution due to local superheating of the solvents leading to local hot spots causing nucleation and crystal growth. Attention must be paid to the choice of appropriate solvents and selective energy input, since starting materials may strongly interact with the MW radiation [7].

Microwave ovens suited for materials synthesis allow one to monitor temperature and pressure during the reaction and thus allow a more precise control of reaction conditions. MW assisted MOF syntheses have mainly focused on (1) the acceleration of crystallization (2) to improve product purity and (3) for selective synthesis of polymorphs. This is due to the direct heating of the solvents and the higher nucleation rate that have been observed. MW assisted synthesis of MOFs has often been carried out at a temperature above 100ºC with reaction times rarely exceeding 1 hr [7].

2.2PHOTOCATAYTIC NATURE

MOFs can be beneficial for making semi-conductors. Theoretical calculations validate that MOFs are semiconductors or insulators with band gaps between 1.0 and 5.5 eV which can be refined by changing the degree of conjugation in the ligands suggesting its possibility for being photocatalysts. The porous channels in MOF structures can be used as photocatalysis sites [6]. Many MOFs exhibit absorption in the ultraviolet region and emissions in the visible region qualitatively similar to semiconductors, while with additional chemical modification of linkers, strong and highly tunable luminescent activities are possible. MOFs can therefore be adapted for a vast variety of optical applications, including luminescent pH sensors, tunable light emitters and photocatalysis [4].

The pollution of surface and ground waters caused by waste waters with a high load of nitrogen compounds like urea, amines, NH_4^+ / NH_3, NO_2^- and NO_3^- is becoming more and more problematic. Large scale animal husbandry and the distribution of inorganic fertilizers are the main source for this. Ammonia emissions are also caused by various other sources like: soda production; nitric acid production; metallurgical industry; coal or biomass gasification. Conventional wastewater treatment plants have only limited capacity for nitrogen removal. Plant effluents thus contain large concentrations of nitrogen, with ammonia being the main form. Nitrogen compounds are often not removed completely in water treatment plants, since the most common biological ways of treatment combining nitrification and denitrification processes often leave one nitrogen species (either NH_4^+ or NO_3^-) in the effluent stream. In natural waters they mainly cause eutrophication. NH_4^+ / NH_3, urea and amines also increase the biological oxygen demand and NH_4^+ / NH_3 is toxic to fish. Occuring in drinking waters NH_4^+ / NH_3 leads to growth of algae and bacteria populations, corrosion of pipes and decreases the level of free available chlorine added for disinfection purposes by the formation of chloramines [3]. Several methods have been proposed for ammonia removal from wastewater such as biological process , stripping [8], ion exchange [9], electrochemical process [10], breakpoint chlorination [11], and photocatalysis [12]. The photocatalytic method for degradation of ammonia is interesting because of its preferences characteristics such as minimal generation of secondary waste, simple operation, remote control, inexpensiveness and high-efficiency [5]. Mozzanega *et.al*. reported the photocatalytic decomposition of gaseous NH_3 under the use of different metal oxides [13],

while Harrison *et.al*. studied the decomposition of NH_3 with photocatalysts (iron doped TiO_2) in acid solution and a degradation of NH_3 without photocatalyst in basic solution with UV-radiation from eight low-pressure Hg lamps was possible [3]. A systematic study of the photocatalytic degradation of different kinds of nitrogen compounds with respect to the mechanisms of their degradation will be necessary.

Photocatalysis using Titanium Dioxide

Semiconducting titanium dioxide (TiO_2), remains the most effective commercially available photocatalytic material. TiO_2 photocatalytic process can generate holes and electrons through TiO_2 excitation by ultra-violet light, and the oxidative holes and reductive electronics involved in the nitrogen balance in wastewater directly. Jianguo Cui and Zhibin Zheng found that after TiO_2 pretreatment NO_2^-/NO_3^- in wastewater was greater than 2 mg/l which was initially 18.7 mg/l. Pretreatment of high concentration ammonia-nitrogen wastewater by TiO_2 photocatalysis can obtain a effluent water with higher and more stable NO_2^-/NO_3^- [8].

pH value and reaction time impact NO_2^-/NO_3^- value greatly pH not only is conducive to $NO_2^-$and NO_3^- photocatalytic reduction, but also can reduce the amount of carbon material in following biological denitrification, and also can reduce the processing cost [8]. Oxidative decomposition of ammonia in neutral (pH) water at 443K is done over Pt/ TiO_2 catalyst to form nitrogen which was indeed analysed during reaction. NH_4^+ / NH_3 to NO_2^- is the rate limiting step in oxidation of NH_4^+ / NH_3 to NO_3^- in presence of common wastewater anions [10]. Oxygen concentration is crucial for selective oxidation of ammonia to nitrogen in liquid phase. Higher concentration leads to over oxidation and hence activity decreases, while at lower concentration activity increases [11]. Kabra *et al*. presented a review on the application of the photo catalytic technique for remediation of inorganic and organic pollutants in wastewater [12].

Photocatalytic process can not only ensure higher and more stable NO_2^-/NO_3^- value, but also convert some ammonia-nitrogen into N_2, therefore it can lighten the burden of following biological denitrification.

TiO_2 can generate holes and electrons by irradiation under ultra-violet light, holes react with OH^- generate •OH, while the electrons react with NO_3^- and NO_2^-, respectively to generate NO_2^- and N_2. The proposed reaction mechanism is as follows[8]:

$TiO_2 + h\nu \rightarrow h^+ + e^-$

$OH^- + h^+ \rightarrow$ •OH

$2 \cdot OH + 2 \bullet OH \rightarrow 2\ H_2O + O_2 \uparrow$

$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$

$2NO_2^- + 6e^- + 8H^+ \rightarrow N_2 \uparrow + 4\ H_2O$

The performance of LECA supported by TiO_2 nanoparticles in the photocatalytic oxidation of ammonia was investigated. The following mechanism was proposed [5]:

$$h^+ + H_2O \longrightarrow H^+ + {}^{\bullet}OH$$

$$NH_3 \xrightarrow{{}^{\bullet}OH} NH_2 + H_2O \xrightarrow{{}^{\bullet}OH} NH + H_2O \xrightarrow{{}^{\bullet}OH} N + H_2O$$

$$NH_x + NH_y \longrightarrow N_2H_{x+y} \xrightarrow{H^+} N_2 \quad (x, y = 0,1,2)$$

$$NH_3 \xrightarrow{{}^{\bullet}OH} HONH_2 \xrightarrow{{}^{\bullet}OH} NO_2^- \longrightarrow NO_3^-$$

The results obtained from photocatalytic treatment experiments of water synthetically polluted with ammonia showed a fairly good performance for the immobilized catalysts. The ammonia was removed (> 85%) within 300 min of the process, and the kinetics of photocatalytic reaction followed a pseudo first order model. The lower limits of the detection for NO_2^- and NO_3^- imply that the hydroxyl radicals serve as the primary reactive species facilitating oxidation of ammonia to nitrogen gas [5].

Titanium based MOF: MIL-125

MIL 125(Ti) or $Ti_8O_8(OH)_4$-$(O_2C$-C_6H_4-$CO_2)_6$ where MIL stands for Material from Institut Lavoisier. MIL-125 synthesised via solvothermal method by Fe`rey et.al. This material, which contains cyclic octamers of TiO_2 octahedra, is photochromic, which is related to the reduction of Ti (IV) to Ti (III) under UV irradiation. Nitrogen sorption experiments reveal that MIL-125 is highly porous with a type I isotherm characteristic of microporous solids, a BET surface area of 1550 $m^2.g^{-1}$, and a micropore volume of 0.65 $cm^3.g^{-1}$[14]. MIL-125 is an active photo catalyst. Doping with elements has been pursued to sensitize photo catalyst with a wide band gap, toward visible light absorption.

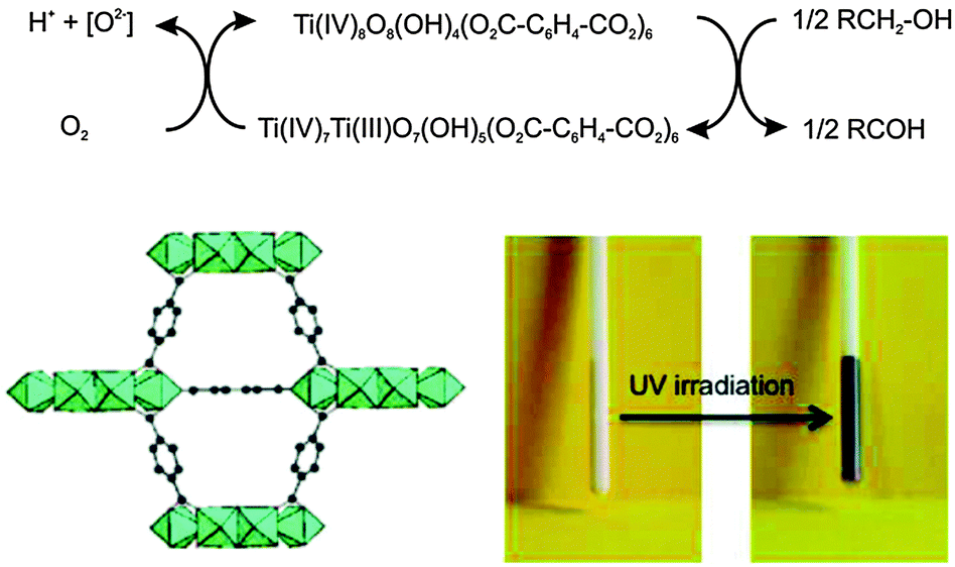


Fig 2.2.1 Alcohol to aldehyde oxidation by MIL-125[14]

Alcohol to aldehyde oxidation has been obtained by MIL-125. The data is in agreement with a longer lifetime of the reduced state within MIL-125 and thus a much higher efficiency of the photo activation than TiO_2 [14].

The degradation of Rhodamine B was used to evaluate the catalytic performance of different systems, where control experiments were conducted to compare the removal efficiencies of RhB by various processes at natural pH with initial RhB concentration of 10 mg/l. After visible light irradiation for 50 min, no observation of the photolysis of RhB in the absence of the catalyst reflects that the RhB was quite stable under visible light irradiation. While

the presence of H_2O_2 could enhance the degradation efficiency of RhB upto 17.6% by photolysis process (H_2O_2 + visible light $\rightarrow$•OH + OH^-) because of the possible H_2O_2 photolysis induced by incident light [15]. With MIL-53(Fe) alone under visible light irradiation, about 62.1% RhB removal was achieved, mainly due to the generation of reactive charge carriers by the excited photoactive MIL-53(Fe), indicating that the synthesized MIL-53(Fe) catalyst possessed moderate photoreactivity [16]. Likewise, we will be following the same protocol for MIL-125.

2.3 METHODS FOR AMMONIA DETERMINATION

For determination ammonia we can perceive the following methods-

Ion chromatography

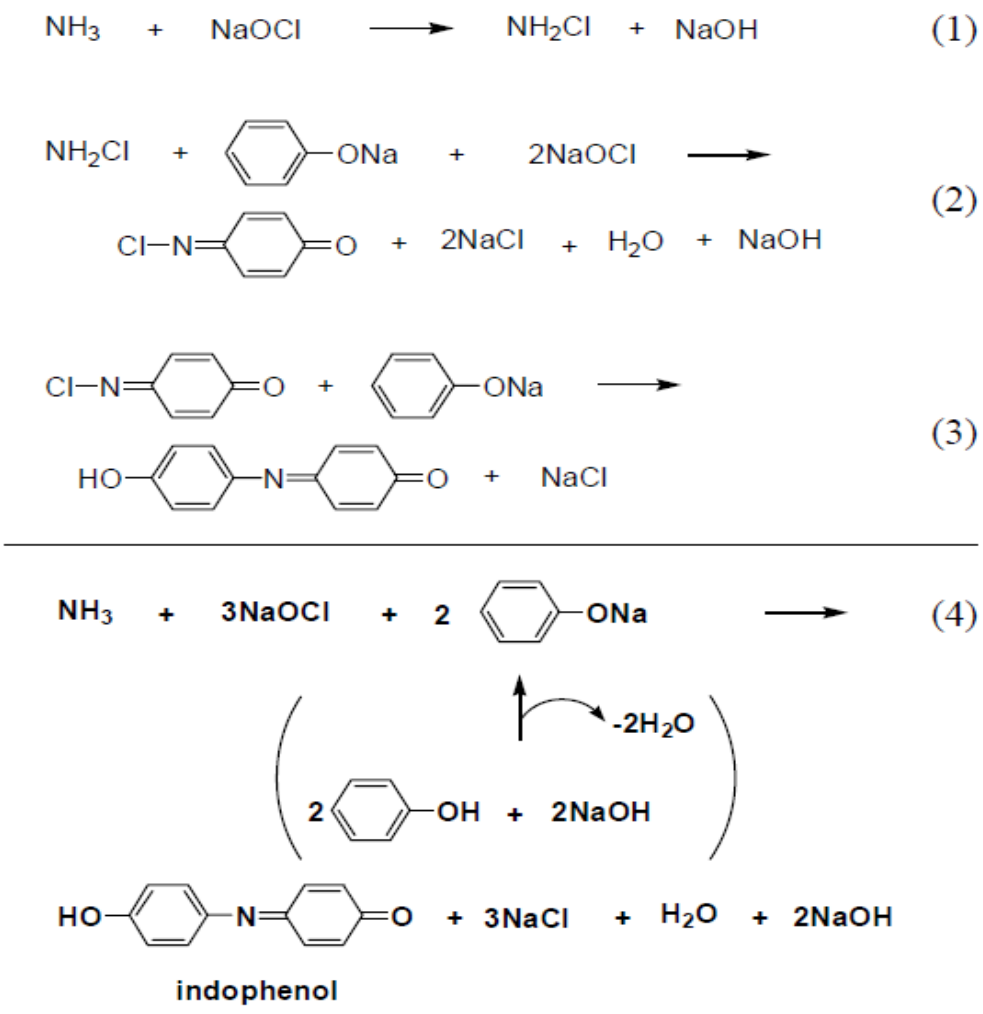
Ion chromatography (or ion-exchange chromatography) is a chromatography process that separates ions and polar molecules based on their affinity to the ion exchanger. This is one of the best method for determination of ammonia in a solution. A buffered aqueous solution known as the mobile phase carries the sample from the loop onto a column that contains some form of stationary phase material. This is typically a resin or gel matrix consisting of agarose or cellulose beads with covalently bonded charged functional groups [17]. Equilibration of the stationary phase is needed in order to obtain the desired charge of the column. If the column is not properly equilibrated the desired molecule may not bind strongly to the column. The target analytes (anions or cations) are retained on the stationary phase but can be eluted by increasing the concentration of a similarly charged species that displaces the analyte ions from the stationary phase. For example, in cation exchange chromatography, the positively charged analyte can be displaced by adding positively charged sodium ions. One of the primary advantages for the use of ion chromatography is only one interaction involved during the separation as opposed to other separation techniques; therefore, ion chromatography may have higher matrix tolerance [18].

Macro-Kjeldahl Method

Principle: In the presence of H_2SO_4, potassium sulfate (K_2SO_4), and cupric sulfate ($CuSO_4$) catalyst, amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined calorimetrically, by ammonia-selective electrode or by titration with a standard acid [19].

4500-NH_3 F Phenate method

The mechanism is as follows:



Principle: Ammonia reacts with phenol to form an intensely blue compound, indophenol, formed by the reaction of ammonia, hypochlorite and phenol catalyzed by sodium nitroprusside. The developed blue color absorbs light of 640 nm wavelength. Hence, lack of intensity in color will show degradation of ammonia [20].

Nessler's reaction method 4500-NH_3 A-C

Named after Julius Nessler, an alkaline solution of K_2HgI_4 is called Nessler's reagent. Crystallizing from a concentrated aqueous solution of mercuric iodide with potassium iodide is the monohydrate $KHgI_3.H_2O$, which is pale orange [21].

Principle: The concentration of ammonia nitrogen in a sample may be determined by the addition of Nessler reagent to the distillate. After allowing time for color development, the color is read at the wavelength between 400-425 nm for a 1 cm path length. The addition of the Nessler reagent $K_2[HgI_4]$ with ammonium will produce a yellow to brown color substituted ammonium salt that is dependent on the concentration of ammonia. The following reaction occurs between ammonium ion and Nessler reagent complex [22]:

$$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \rightarrow HgO{\cdot}Hg(NH_2)I \downarrow + 7I^- + 3H_2O$$

It also acts as a stopping agent for reaction in solution. The amount of color is a function of the concentration of ammonium-nitrogen. By monitoring the color change from the Nessler's reagent, the concentration of ammonia may be determined.

Spectrophotometric EPA Method 354.1 for nitrite estimation

This method is for the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes. The method is applicable in the range from 0.01 to 1.0 mg NO_2^-N/l.

Principle: The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.

Spectrophotometer equipped with 1 cm for use at 540 nm. Samples should be analyzed as soon as possible, otherwise, may be stored, but for 24 to 48 hours at 4°C.

There are very few known interferences at concentrations less than 1,000 times that of the nitrite. However, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (>600 mg/l) will give low results due to a shift in pH. Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

Method for preparation of Buffer-color reagent:
Add 105 ml conc. hydrochloric acid, 5 g sulfanilamide and 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride to 250 ml of distilled water. Stir until dissolved. Add 136 g of sodium acetate and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark [23].

The research is emphasised on application of microwave synthesized MIL-125 as a potential photo catalyst. Mainly, the focus will be on degradation of ammonia in wastewater. The benchmark catalysts ZnO and TiO_2 will also be used. A kinetic modelling is requisite for estimation of efficiency.

III. EXPERIMENTAL WORKS

This chapter explains the miscellaneous materials and resources utilized and the experimental protocols followed. The chapter is segregated into seven main sections to ameliorate explanation sequentially and logically. An overarching description to all the following sections are explicated below.

3.1 CHEMICALS AND INSTRUMENTATION

Chemicals

The chemical reagents used were of analytical grade and acquired from commercial sources. The chemicals utilized are as follows:

Table 3.1 Chemicals used

Chemicals	Molecular Formula	Manufacturer
Ammonium Sulphate	$(NH_4)_2SO_4$	Fischer Scientific
Conc. Hydrochloric acid	HCl	Ranbaxy Fine Chemicals
Deionized water (15MΩ)	H_2O	Millipore milli-Q instrument
DMF or N, N-dimethylformamide	C_3H_7NO	Emplura
Ethanol	C_2H_5OH	Merck
Ferric Chloride or Iron (III) chloride anhydrous	$FeCl_2$	Merck
Methanol	CH_3OH	Ranbaxy Fine Chemicals
Methylene blue dye	$C_{16}H_{18}ClN_3S$	Merck
n,n-Naphthyl ethylene diamine dihydrochloride	$C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCl$	LOBA Chemie
Nessler Reagent or Potassium tetraiodomercurate(II)	$K_2[HgI_4]$	Nice chemicals

Sodium Acetate	CH_3COONa	Fischer Scientific
Sodium Nitrite	$NaNO_2$	Fischer Scientific
Sulfanilamide	$C_6H_8N_2O_2S$	Nice Chemicals
Terephthalic acid or 1,4-benzene dicarboxylic acid	$C_8H_6O_4$	LOBA Chemie
Titanium Dioxide	TiO_2	Fischer Scientific
Titanium Isopropoxide	$Ti(OiPr)_4$	Otto Chemie
Zinc Oxide	ZnO	Fischer Scientific

Various Equipment and Instruments used

The major synthesis of MIL-125 was performed using Microwave reactor (Monowave 300, Anton Paar). A hot air oven where temperature upto 210°C is achievable. The distinguished characterization techniques that were adopted for analysis were SEM, Powder XRD, TGA, BET surface area analysis, FTIR and UV reflectance analysis. The images, for exploring the morphology of MOF crystals were taken via scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The samples were gold-coated for conductivity, helping to get a better image. The crystalline phase of the MOF powders were determined using an X-ray diffractometer equipped with the graphite monochromatized CuKα radiation (λ=1.5406 Å) in 2θ angles ranging between $5^o<2\theta<50^o$ at room temperature. Thermal analysis was carried out in detail in a TGA apparatus, Shimadzu (DTG 60 H). BET surface area analysis was performed by a surface area analyzer (Autosorb-1, Quantachrome) at liquid N_2 temperature of 77 K. The relative pressure in BET surface area calculation was taken between 0.05-0.35. FTIR of MOFs was performed in ThermoFicher Nicolate IS-10, from 500cm^{-1} to 4000 $cm^{-1}$with bandwidth of 0.5 nm. Furthermore, the quantitative estimation of concentration in all photocatalytic experiments was carried out in a UV-*vis* spectrophotometer (Jasco, V-530). Also, the band gap analysis of synthesised MOFs was calculated from the data obtained using UV diffused reflectance spectroscopy *via* the same UV-*vis* Spectrometer.

3.2 SYNTHESIS OF MIL-125 VARIANTS

Microwave synthesis of MIL-125

A batch of MIL-125 was prepared in accordance to the procedure given by Hongxu Guo Et. Al. 0.498 g (3 mmol) of Terephthalic acid and 0.6 ml (2 mmol) of Titanium Isopropoxide i.e. $Ti(OiPr)_4$ were added, respectively to a solution of 15ml of n,n-dimethylformamide i.e. DMF and 2 ml of methanol. Titanium Isopropoxide has to be injected in methanol first, mixed and then added to DMF. The mixture was stirred gently for 20 min at room temperature, and then transferred into a 30ml microwave synthesis reaction vial. The microwave was kept at requisite temperature and time at 500 rpm, en route pressure varies with maximum reaching 12 bars. The mixture is allowed to cool to room temperature after the reaction. The precipitates were washed twice with DMF and then deionized water and centrifuged and dried at 150°C for 24 hr each time after each wash. The product is then kept at 200°C for calcination to obtain the final off-white powder [16].

Fig 3.2.1 Microwave Reactor and reaction vial used for microwave synthesis

Microwave synthesis of Fe doped MIL-125

The synthesis of Fe doped MIL-125 followed the same protocol as mentioned above but with addition of Iron (III) chloride anhydrous which is taken as 10% of Titanium Isopropoxide (i.e. 0.2 mmol), befitting the stoichiometry.

Solvothermal Synthesis of MIL-125

The reaction mixture is same for this synthesis as mentioned in 3.2.1. Here, the reaction mixture, rather than filling into a microwave vessel is filled into the Teflon tubes which are indeed fitted into an autoclave. The reaction time is 8 hours and temperature is kept at 150°C. After reaction, the autoclave is allowed to cool for 3-4 hours. The product is then subjected to post treatment and storage.

Fig 3.2.2 Autoclave used for Solvothermal synthesis

3.3 OPTIMISATION OF PARAMETERS FOR SYNTHESIS

Following the above protocol, the synthesis routes using for MIL-125 had to be optimized for yielding product of good reproducibility and optimum quality effective in photocataysis. The reactant/solvent molar ratio was kept constant. Stirring time, reaction time and temperature were the controllable parameters undertaken. Following table 3.3.1 shows optimization with time and temperature as variable parameters.

Table 3.3.1: Time and temperature as variable parameters

Time / Temp	20 min	40 min	60 min	80 min
100 ºC	✓	✓	✓	✓
120 ºC	✓	✓	✓	✓
150 ºC	✓	✓	✓	✓

3.4 BULK SYNTHESIS

After characterization of MIL-125, bulk synthesis was carried out for stirring time of 20 min at 120°C with 40 min as holding time in microwave synthesis reactor. It was collected and subjected for washing with water and dried. Around 20 batches were prepared and water washed together for 24 hours. The yield after post treatment was found to be 82.93 %.

3.5 AQUEOUS PHASE STABILITY

As a priori, the aqueous phase stability of synthesized MIL-125 was experimentally observed before ascertaining its photocatalytic prowess. The material was weighed (approximately 200 mg) into 5 sets and solutions of variable pH range viz 2, 4, 7, 9 and 11 were made using milli pore water. These solutions were then filled into respective 30 ml borosilicate glass tubes. The pH of respective solutions was maintained using standard buffer solutions and accuracy was measured time to time using glass electrode pH meter. The 5 bottles were subjected to stirring using magnetic stirrer for 5 hours at ambient temperature. After 5 hours, solutions are allowed to settle and the supernatant is dispensed**.** The remaining quantity of respective bottles is centrifuged at 6000 rpm for 15 minutes and kept in hot air oven at 150 ˚C for drying and stored in vaccum for further characterization.

3.6 STUDY ON PHOTOCATALYTIC EFFECT OF MATERIAL

The fig 3.6.1 shows the schematic of experimental setup incorporated for photocatalytic studies. The experimental setup consists of a High pressure mercury vapor lamp (125 W) as the artificial light source for photo catalytic degradation. The light was directed to a sealed conical flask (100 ml) made of Pyrex glass. This lamp is concealed in wooden box wrapped with reflective sheet and has a door to it. This acts as a visible UV light chamber. The chamber is kept over a magnetic stirrer for purpose of agitation of solution in flask. The agitation rate can be controlled using the controller knob in magnetic stirrer. The HPMV lamp and magnetic stirrer both are connected to an A.C. Source.

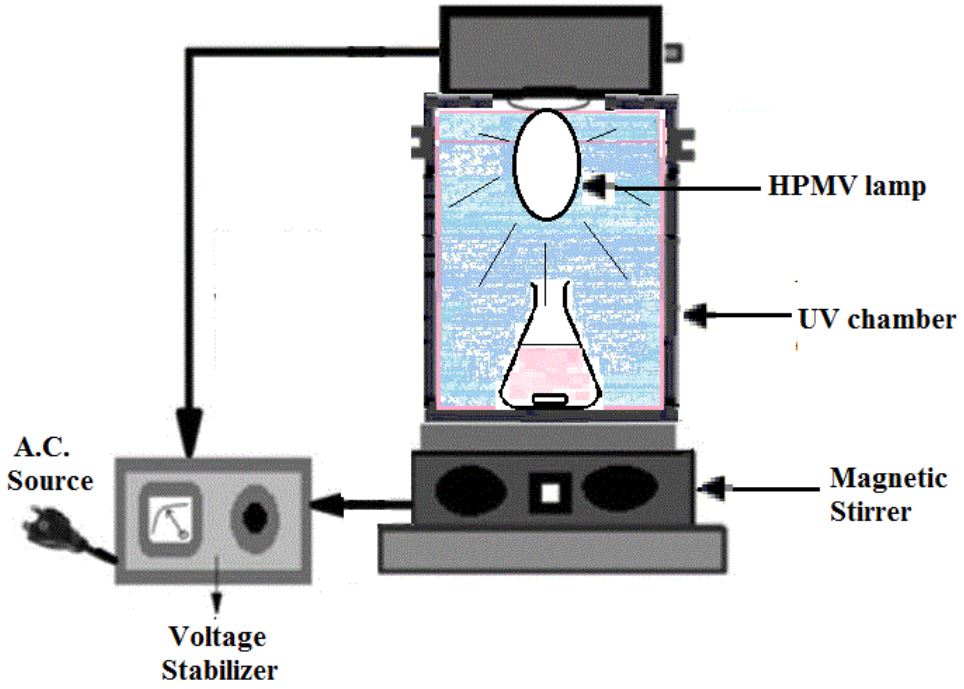


Fig 3.6.1 The schematic of experimental setup

To prove the photocatalytic activity of synthesized material, photodegradation of methylene blue was carried out according to the protocol as follows:

Methylene blue dye is the most basic dye used for preliminary investigation of measuring photocatalytic activity. The 20 ppm solutions of methylene blue dye is used for this study. The amount of catalyst used is 20 mg common for all systems. This dye on dissolving in water shows λ_{max} at 664 nm at STP. The experimental sets were as mentioned in table below.

Table 3.6.1 Experimental conditions during photocatalytic study

Sl.No.	Dye	Catalyst	Conditions
1.	✓	-	Dark
2.	✓	✓	
3.	✓	-	Light
4.	✓	✓	

3.7 DEGRADATION OF AMMONIA

Nessler Reaction Method.4500-NH_3 A-C

For photo catalytic degradation of ammonia in water, standardization is to be carried out using UV spectrophotometer at 425 nm for determining concentration values[See Appendix].

The same experimental setup was used as mentioned above. The ammoniacal solutions of known concentrations were filled in conical flask of 100 ml alongwith known quantity of material and subjected to irradiation under High pressure mercury vapor lamp over a time till steady state of the system is achieved. *Nessler Reaction Method.4500-NH_3 A-C* was followed for detection of ammonia. The samples are analysed in UV spectrophotometer for absorbance at 425 nm and likewise final concentration is deduced.

These are placed under High pressure mercury vapor lamp. For each 1 hour interval, samples (2 ml) are taken out in appendorf tubes and centrifuged. 1 ml is taken and diluted with milli-q water and 0.4 ml Nessler reagent is added and mixed well. This is kept in dark for 20 minutes for solution to stabilize and attain uniform colour and later on it is analysed in UV spectrophotometer for absorbance at 425 nm. Experiment is prolonged upto 4 hours. Titanium Dioxide and Zinc oxide are taken as the benchmark material.

Spectrophotometric EPA Method 354.1 method

The nitrite estimation is done using buffer color reagent from *Spectrophotometric EPA Method 354.1* method. For each 1 hour interval, samples (2 ml) are taken out in appendorf tubes and centrifuged. 1 ml is taken and diluted with milli-q water and 2 ml of buffer color reagent is added and mixed well. This is kept in dark for 15 minutes for solution to stabilize and attain uniform colour and later on it is analysed in UV spectrophotometer for absorbance at 540 nm. Simultaneously, the same sample were analysed for ammonia detection using *Nessler Reaction Method.4500-NH_3 A-C.*

IV. RESULTS AND DISCUSSION

This section details about the various findings we came across while carrying out various procedure of synthesis authenticated by characterization and the experiments.

4.1 CHARACTERIZATION OF MIL-125

All synthesized MIL-125 were characterized using standard methods *viz*. SEM, PXRD, TGA, BET surface area analysis, FTIR and UV reflectance analysis.

4.1.1 Scanning Electron Microscopy Images

This SEM images are after complete water washing for 24 hours so as to obtain fine crystalline nature and remove any non requisite solvents. The size and shape though varied from sample to sample. For the sake of brevity, the images at different magnification and resolution were not shown here.

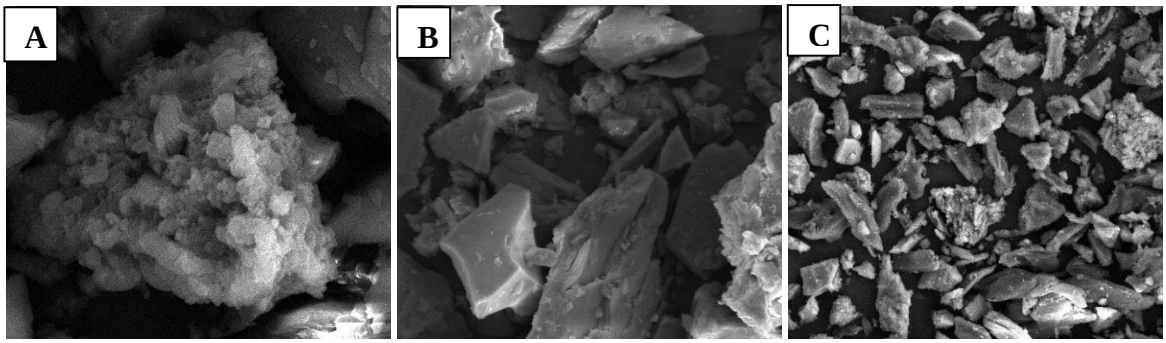


Fig 4.1.1.a SEM images of MIL-125: Stirring Time (**A)** 20 min **(B)** 300 min**(C)** 3600 min

From the fig 4.1.1.a, observations was made on the crystalline morphology of MIL-125 under various stirring time. It was observed that at stirring time of 20 min itself, gives uniform crystalline structure.

SEM images for the optimization of MIL-125 under two variable parameters can be observed, viz. synthesis temperature and synthesis time, respectively.

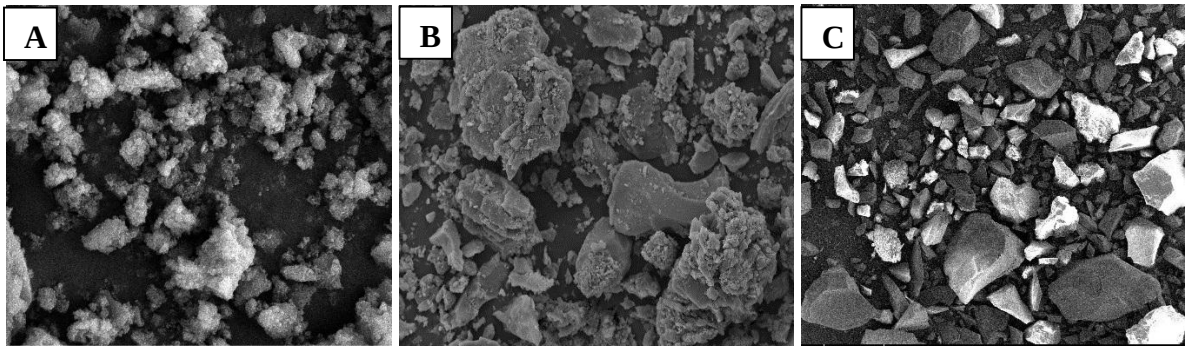


Fig 4.1.1.b SEM images of MIL-125: Temperature range **(A)** 100°C **(B)** 120°C **(C)** 150°C

The SEM image for MIL-125 at 120°C shows more crystalline nature.

In fig 4.1.1.c, the images of MIL-125 MW and MIL-125 Solvothermal shows more breathing and crystalline morphology. It also shows the samples consist of well crystalline block-like particles with various shapes.

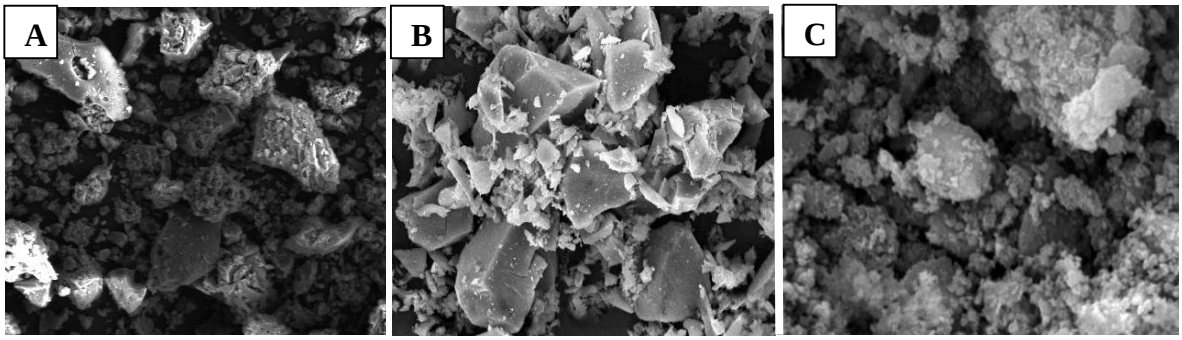


Fig 4.1.1.c SEM images of MIL-125**:**

(A) MIL-125 MW **(B)** Fe doped MIL-125 **(C)** MIL-125 Solvothermal

4.1.2 EDX Analysis

EDX is the Energy Dispersive X-ray spectroscopy helpful in finding out the elemental content in a sample. From figure 4.1.2, we can observe that the product EDX shows presence of Ti, C and O, likewise compound has a $(Ti_xC_yO_z)_a$ composition. This EDX spectrum, hence, also shows the absence of other metallic impurities and hence high product purity.

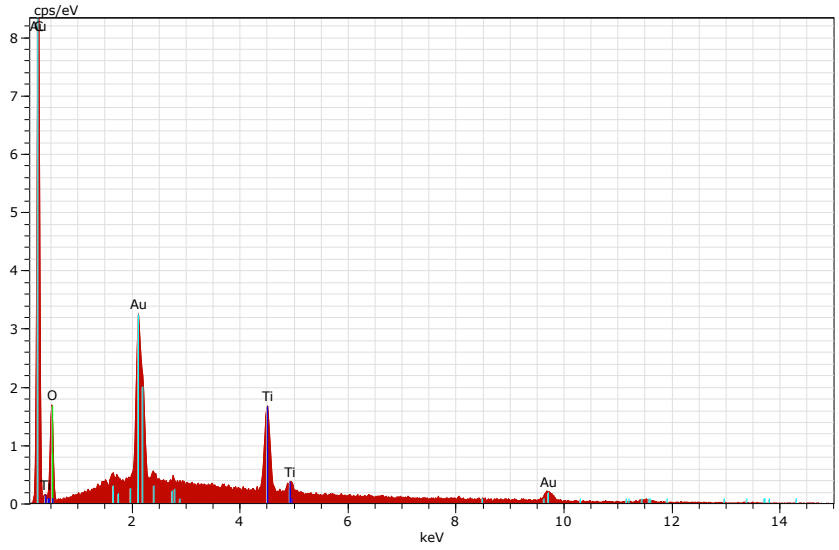


Fig 4.1.2 EDX graph analysis for MIL-125

Table 4.1.2 Composition of MIL-125 using EDX spectrum

Element	Atomic Number	Atom. C [wt.%]
C	6	68.34
O	8	26.69
Ti	22	4.97

4.1.3 Aqueous Phase Stability study

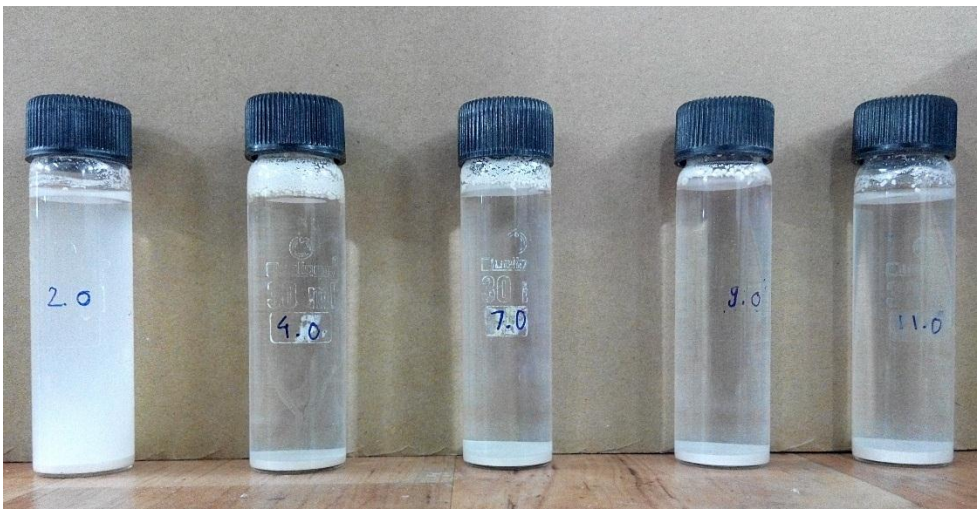


Fig 4.1.3 Digital images of various systems during pH interaction study

Here, it can be observed that acidic pH (especially 2 pH in this case) leads to diffusion of MIL-125 and turbidity of solution as presence of H^+ ions is in excess and their interaction with Titanium core. Though structural integrity cannot be established on optical image source.

4.1.4 XRD Analysis

The powder XRD patterns (Fig 4.1.4.a) corroborated the crystallinity of the synthesized MIL-125. Comparisons with other patterns of different conditions, viz. three different synthesis time 20 min, 40 min and 60 min in accordance to three different temperatures 100°C, 120°C and 150°C, respectively is achieved. MIL-125 synthesized at 120 °C for 40 min shows the sharp pattern with the least distortion and a pattern of a highly pure crystalline product. The presence of sharp peaks was found to be consistent with the database and reported literature. While the rest synthesized products are showing lack of crystallinity and amorphous natures.

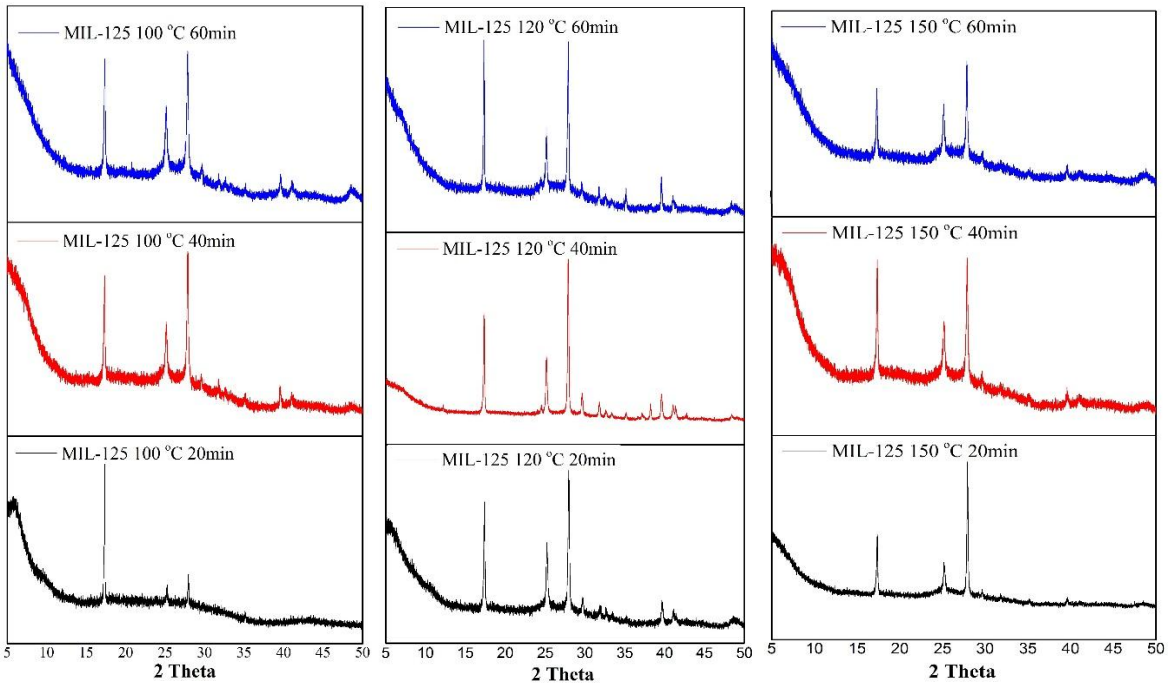


Fig 4.1.4.a PXRD pattern for different conditions incurred during optimization

Fig 4.1.4.b is the ideal PXRD pattern we obtained for MIL-125 synthesized at 120°C with reaction temperature of 40 minutes. The presence of sharp peaks was found to be consistent with the database and reported literature. For this particular condition all PXRD peaks were well indexed

with space group I 4/mmm and unit cell parameters of a=9.832 Å, b=9.832 Å, c=15.345 Å, α=90º, β=90º and γ=90º. The same will be used as a reference for other experiments.

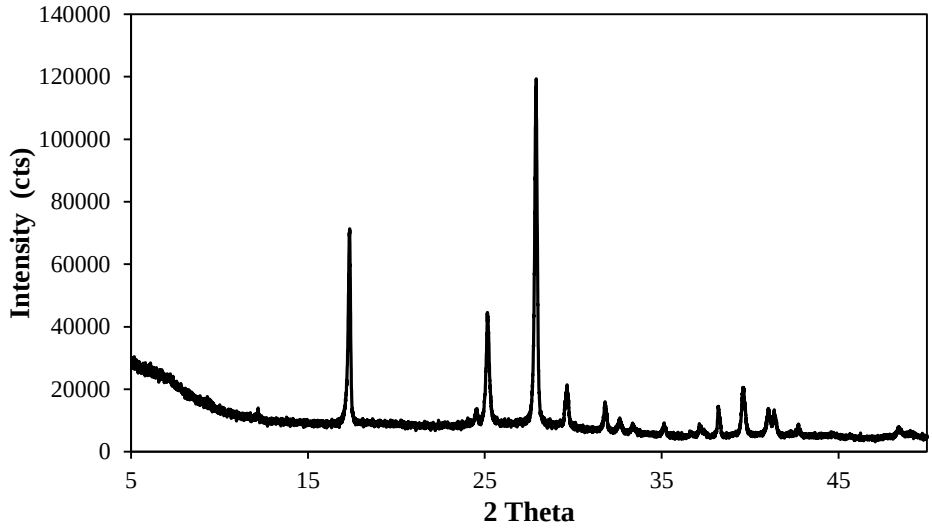


Fig 4.1.4.b Powder XRD pattern of MIL-125

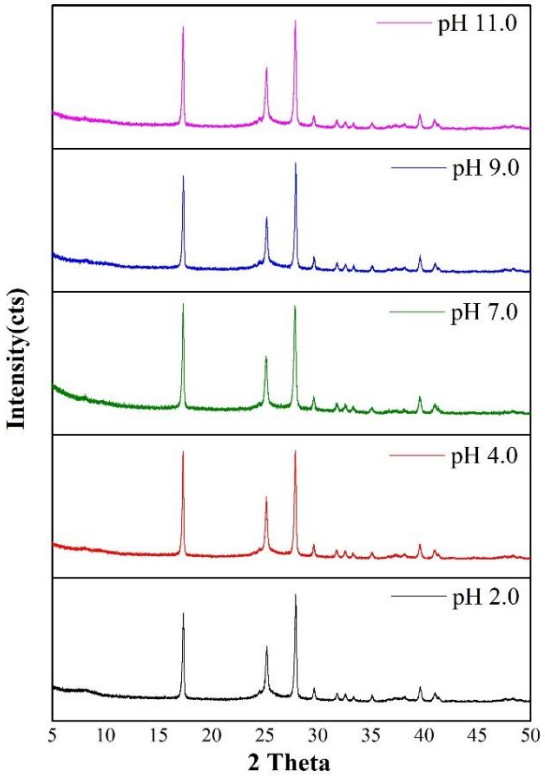


Fig 4.1.4.c PXRD pattern of MIL-125 for different ph environments

The patterns obtained in fig 4.1.4.c are the PXRD patterns for the various systems of pH incurred during study of aqueous phase stability of MIL-125. These are found to be matching the reference PXRD pattern of MIL-125 from bulk synthesis. Thus, it can be concluded that MIL-125 has a high aqueous phase stability in wide pH range

4.1.5 Fourier Transform Infra-Red Spectroscopy

The Fig 4.1.5, shows the FTIR spectra of Ti based MOF *via* three synthesis viz MIL-125 MW, Fe doped MIL-125 and MIL-125 Solvothermal each with 40 min of synthesis time. The fingerprint region (i.e. ῡ <1500 cm^{-1}) is found to be very similar to MIL-125.The peaks in FTIR spectra shows a substantial increase in intensity indicating the repetition of same functional groups. The peaks at 1677 cm^{-1} and 1281 cm^{-1} is associated with the presence of dicarboxylate linker in synthesised material. The region in between 1680 to 1400 cm^{-1}, relates to O-C-O asymmetric and symmetric stretching of carboxylic acids. The peaks around 850 cm^{-1} is assigned to Ti-O stretching for non-bound oxygen atom. While peaks at 780,680 and 560 cm^{-1} is associated with Ti-O-Ti stretching vibration. The peak at 525 cm^{-1} in the FTIR of Fe doped, shows Fe-O stretching.

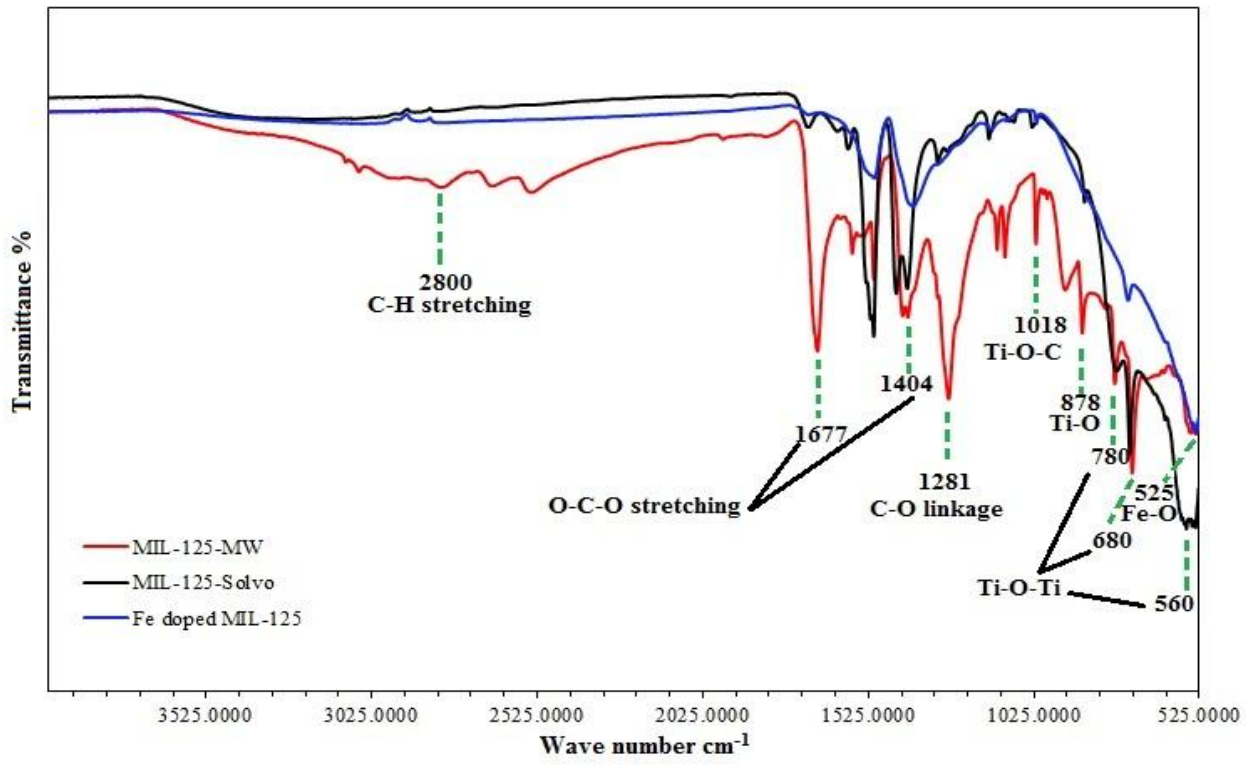


Fig 4.1.5 FTIR Spectra of MIL-125 MW, Fe doped MIL-125 and MIL-125 Solvothermal

4.1.6 Thermo Gravimetric Analysis

The TGA profiles were shown in Fig 4.1.6.a. It can be deduced that MIL-125 is thermally robust. The profile clearly illustrated the degradation temperature of MIL-125 which would be helpful in fixing its usable limit in various catalytic applications. The TGA was carried out at room temperature to 700°C at 10°C/min with O_2 atmosphere. The slight decrease in mass % from 100°C to 150°C resembles the weight loss of solvents viz. water and DMF. During the departure of the guest molecules below 200 °C followed by thermal gravimetric analysis, X-ray thermodiffractometry does not indicate any change in crystallinity. A phase transition occurs between 337 °C and 470 °C, characterized by a strong change in peak positions and a decrease in crystallinity, before the collapse of the solid above 340 °C[14].

The DSC (Differential Scanning Calorimetry) data in fig 4.1.6.b, shows the nature of reaction i.e. peak ranging from 370 ºC to 500 ºC resembles exothermic nature accompanied with phase transition. It can be assumed that the oxidation of BDC occurs within these range. The structural reorganization at ca. 385 °C is probably related to the departure of hydroxo groups, evidenced by the small weight loss of 4-5% at this temperature range[14].

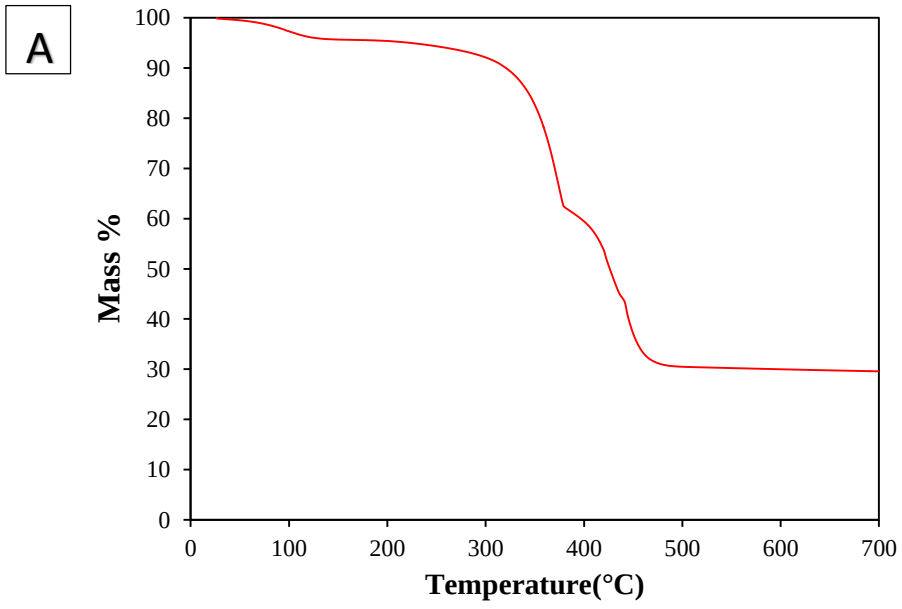


Fig 4.1.6 (A) TGA data for MIL-125

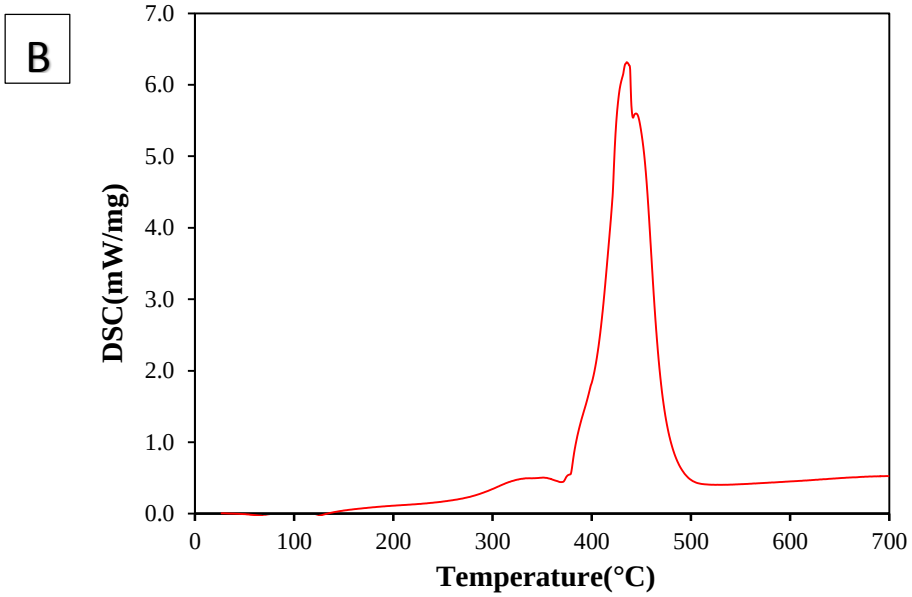


Fig 4.1.6 (B) DSC data for MIL-125

4.1.7 BET Surface Area Analysis

After TGA report, the outgassing temperature could be well determined. The reported BET surface area found to be in the order as, MIL-125 MW > Fe doped MIL-125 >MIL-125 Solvothermal indicating highly porous nature of samples.

Table 4.1.7 BET Surface Area of catalyst

Catalyst	Surface Area (m^2/g)
MIL-125 MW	371.9
MIL-125 Solvothermal	240
Fe doped MIL-125	246.1

4.1.8 Diffused UV reflectance analysis

The wavelength range under study was the UV-visible region of electromagnetic spectrum. The calculation details for band gap measurement was on the basis of K-M model. Followed by the application of Kubelka –Munk transformation of reflectance.

$K = (1-R)^n /2R$

Where, K is the reflectance transformed according to Kubelka –Munk, R is the reflectance.

n = 2, for direct electronic transition

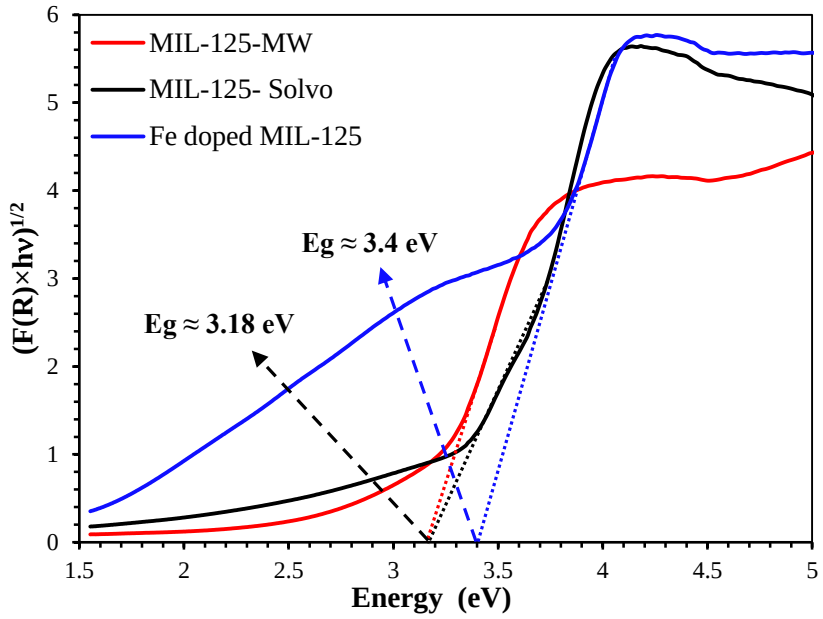


Fig 4.1.8.a Diffused UV reflectance Spectra of MIL-125 via different synthesis route

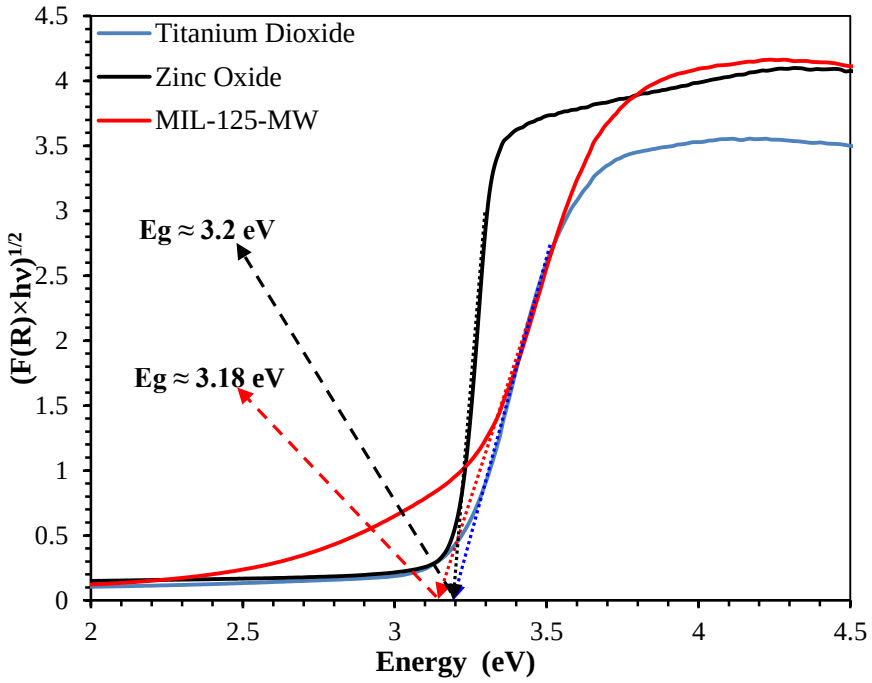


Fig 4.1.8.b Diffused UV reflectance Spectra of MIL-125 and benchmark catalysts

Fig 4.1.8.a shows Diffused UV reflectance Spectra for MIL-125 MW, Fe doped MIL-125 and MIL-125 Solvothermal. Fig 4.1.8.b shows Diffused UV reflectance Spectra for TiO_2, ZnO and MIL-125. The data obtained for MIL-125 MW showed band gap energy of 3.18 eV, falling in the visible region of electromagnetic spectra. The threshold wavelength was determined to be 390 nm, below which MIL-125 exhibits photocatalytic activity.

Table 4.1.8: Band gap energy of catalyst

Sl. No.	Catalyst	Band gap energy(eV)	Threshold Wavelength(nm)
1.	MIL-125 MW	3.18	390
2.	Fe doped MIL-125	3.4	365
3.	MIL-125 Solvothermal	3.18	390
4.	Titanium Oxide	3.18	390
5.	Zinc Oxide	3.2	388

Table 4.1.8 encapsulates the band gap energy of the analysed catalysts. The result for MIL-125 MW obtained was similar to that reported in literature. The light source used for photocatalytic reactions is high pressure mercury vapour lamp whose wavelength spectra lies within visible and low UV region of EM spectra is proposed to be the adequate light source.

4.2 PHOTOCATALYTIC EFFECT

4.2.1 Controlled experiments

First controlled experiment was designed to show the effect of light on the dye subjected to degradation alone. The results showed that on exposure to light, MB had no change in its λ_{max} value neither change in its position or intensity. Hence it can be inferred that the dye is photosensitive.

Second controlled experiment was to estimate the effect of the material synthesized on the dye in the dark. It was visually observed that the material synthesized is of off white colour. As the material is exposed to dye in the dark, the colour of the material changes to blue. UV absorbance analysis showed drop in intensity of λ_{max} , but no shift in λ_{max} position, pointing to the fact that the process is completely physical adsorption.

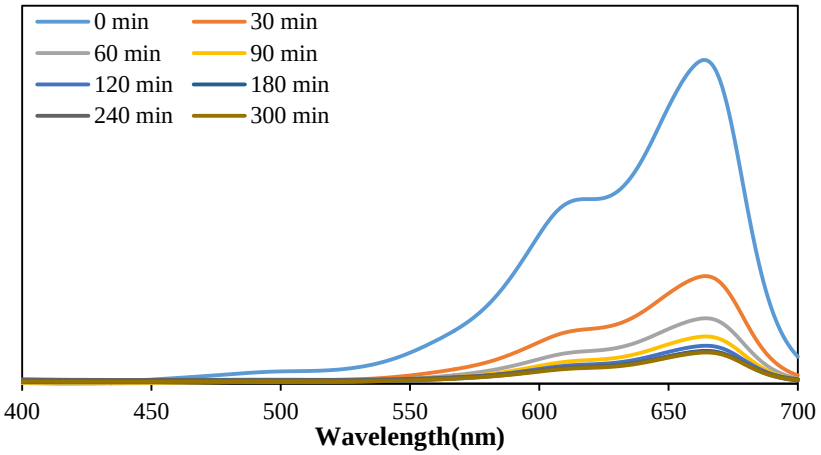


Fig 4.2.1.a UV Absorbance profile for adsorption of MB solution

In presence of visible light irradiation, as time proceeds the λ_{max} shifts, showing change of colour from blue to pale violet then colourless. Similar observations was found on the material synthesized. The blue colour formed due to the adsorption of the surface of the material gradually fades to white as observed before adsorption. Then proving without any doubts that the dye has been completely degraded. Thereby proving the photocatalytic activity of the material.

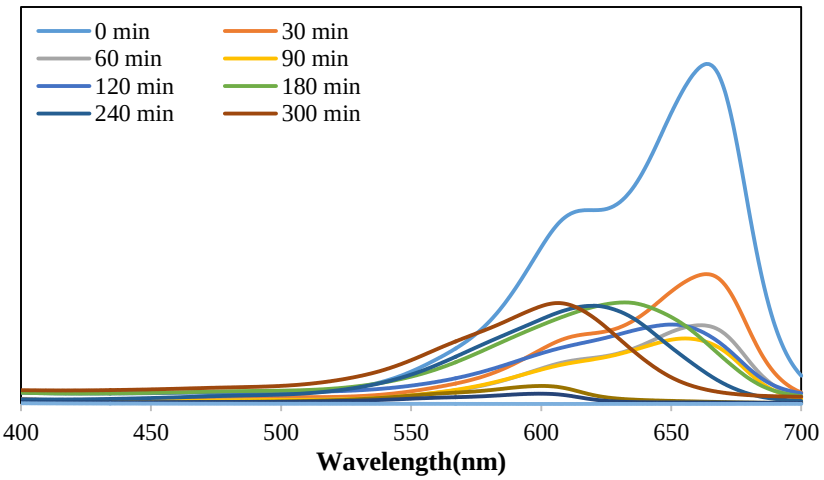


Fig 4.2.1.b UV absorbance profile for degradation of MB solution

Similar observation and inferences was drawn for the bench mark photocatalyst as well as for the Iron doped MIL-125 and MIL-125 Solvothermal in study.

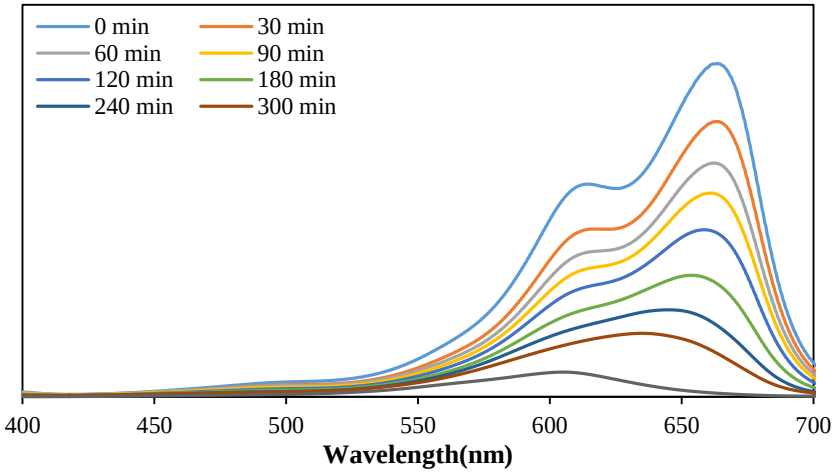


Fig 4.2.1.c UV absorbance profile for degradation using Fe doped MIL-125 MOF

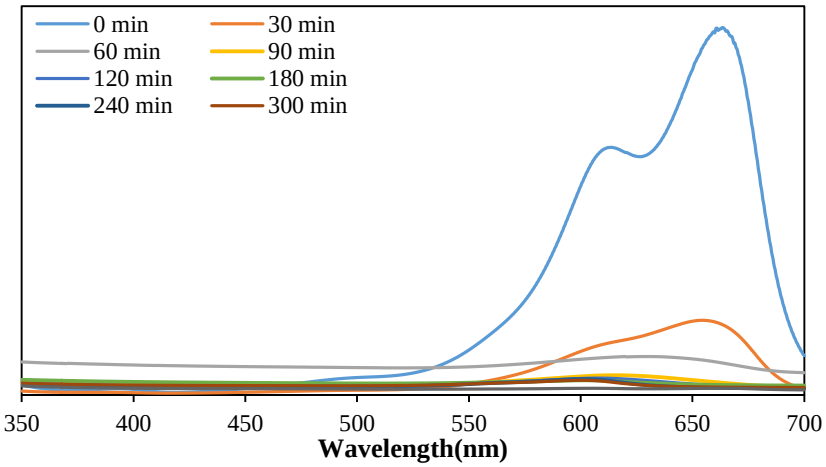


Fig 4.2.1.d UV absorbance profile for degradation using MIL-125 Solvothermal

In fig 4.2.1.e, the visual evidence of methylene blue dye degrading over time duration of 6 hours can be observed. For the sake of brevity the best of the results are displayed in respective figure.

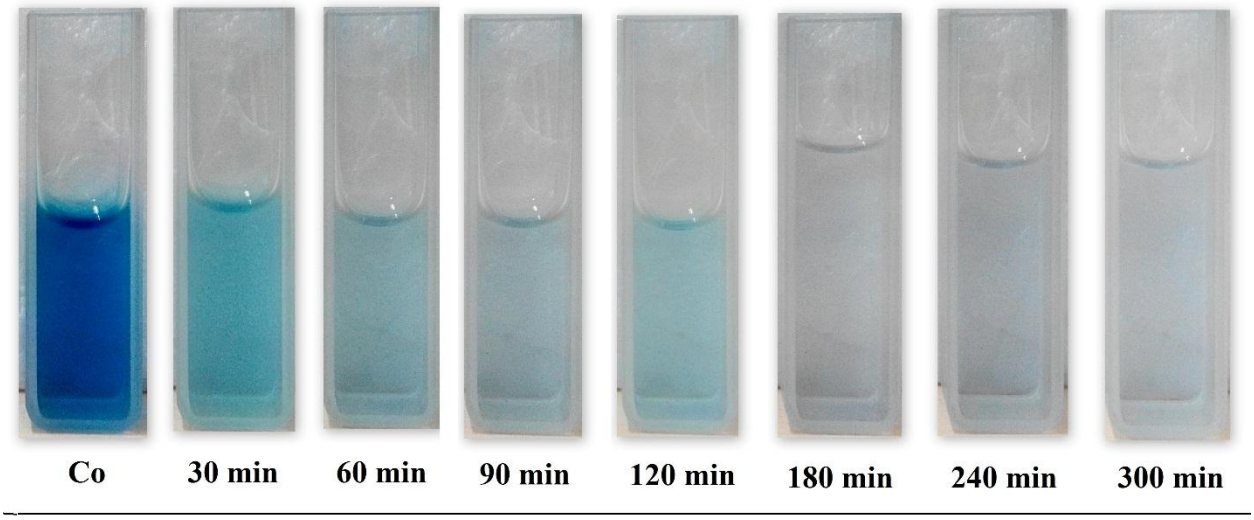


Fig 4.2.1.e Digital images of MB solution degradation over time duration

The concentration profile for all the Titanium based catalyst used in this project is shown in fig below. The degradation was found to be in the order as: MIL-125 Solvothermal > TiO_2 > MIL-125 > Fe doped MIL-125.

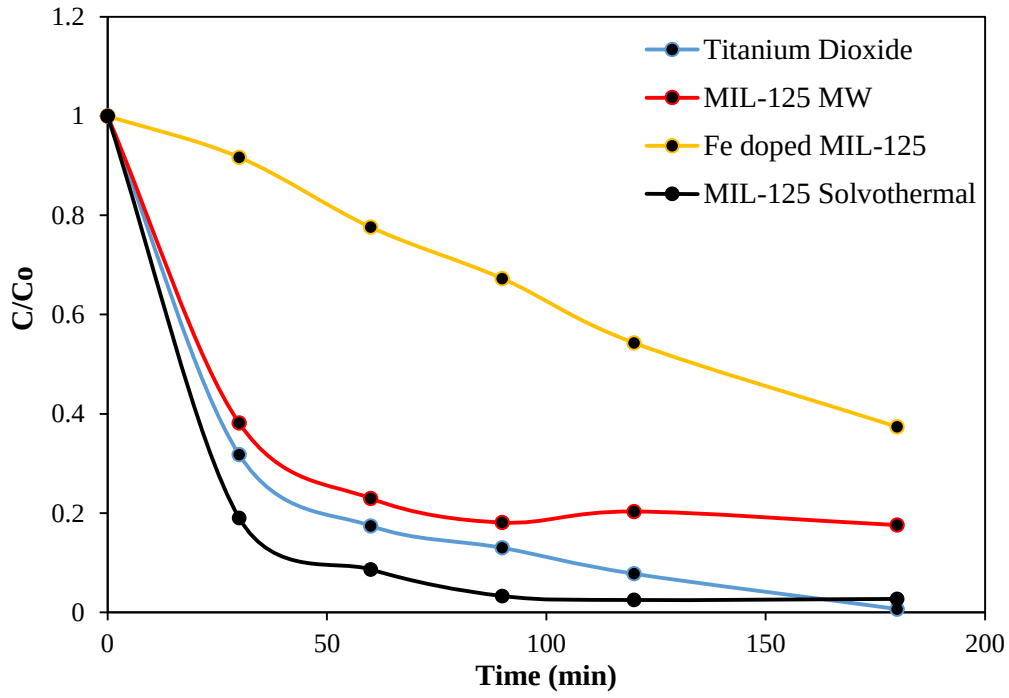


Fig 4.2.1.f Concentration profile for MB solution using Titanium dioxide, MIL-125 MW, Fe doped MIL-125 and MIL-125 Solvothermal

The reaction mechanism of overall dye decolorization can be based on semiconductor theory. On exposure to photons with energy equal to or greater than the band gap energy of catalyst excites electrons from the valance band to the conduction band and thereby produces holes in the valance band. The photo generated holes with strong oxidant capacity can directly oxidize adsorbed organic molecules (as in this case, the dyes) or react with water molecules or hydroxyl ions to generate hydroxyl free radicals. The free formed hydroxyl radicals can also oxidize said organic molecules. Meanwhile, photo generated electrons can be trapped by molecular oxygen to form superoxide radical, which also possess strong oxidizing ability to decolorize dyes. The low photo generation efficiency could be due to fast electron-hole recombination. Consequently, the electron of the excited state decays to the ground state after electron transfer.

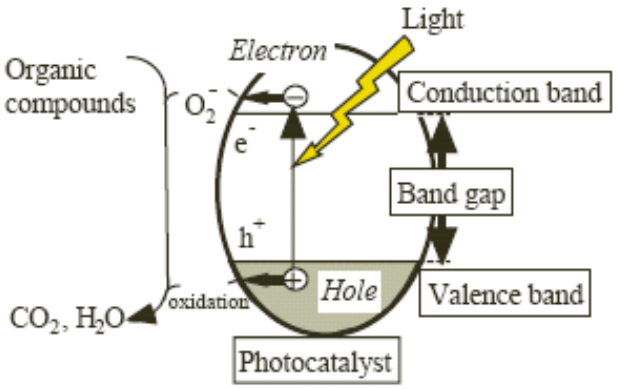


Fig 4.2.1.g Mechanism of photocatalysis [24]

4.2.2 Degradation of Ammonia

The proposed application is to study the degradation of ammonia in presence of MOFs and two benchmark photo catalysts (TiO_2 and ZnO). The breakdown temperature of MOFs could be referred back to Fig 4.1.6.(A). The reaction kinetics was carried out only in the narrow range of temperature (*room temperature*). From the Fig 4.2.2.a, it could be inferred that, the reaction followed pseudo first order. The first-order kinetics can be written as $\ln (C_O/C) = kt$ which is similar to $C = C_O \exp(-kt)$ according to the Langmuir–Hinshelwood model [24].

The proposed kinetic model focusses on the feasible products in the oxidation and reduction pathway of ammonia [6] as in equation (A) & (B). From the fig 4.2.2.a, $k_{overall}$ (k_{123}) for each can be determined using the curve fitting of the acquired plots.

$$NH_4^+ \xrightarrow{k_{123}} \text{Products} \qquad \text{(A)}$$

$$NH_4^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2^- \qquad \text{(B)}$$

$$NH_4^+ \xrightarrow{k_3} N_2$$

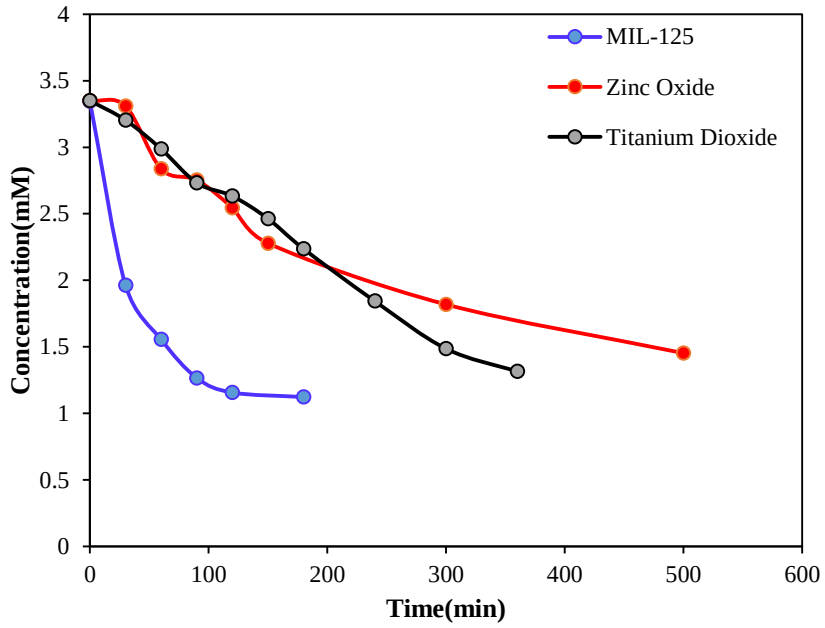


Fig 4.2.2.a Concentration profile for degradation of ammonia using MIL-125, Zinc Oxide and Titanium Oxide

Table 4.2.2: $k_{overall}$ of Photo catalysts for Ammonia degradation

Sl.No.	Catalyst	$k_{overall}$ (min^{-1})
1.	MIL-125	0.03189
2.	Titanium Oxide	0.0031
3.	Zinc Oxide	0.0035

From the above Table, it can be understood that MIL-125 is clearly an outstanding photo catalyst in ammonia degradation with kinetic factor 10 times more than the conventional benchmark of Zinc Oxide and Titanium Oxide. The percentage degradation of ammonia was found to be 66.47% for MIL-125, while for conventional catalysts such as Zinc Oxide and Titanium Oxide was found to be 53.48% and 33.25% respectively for 180 min.

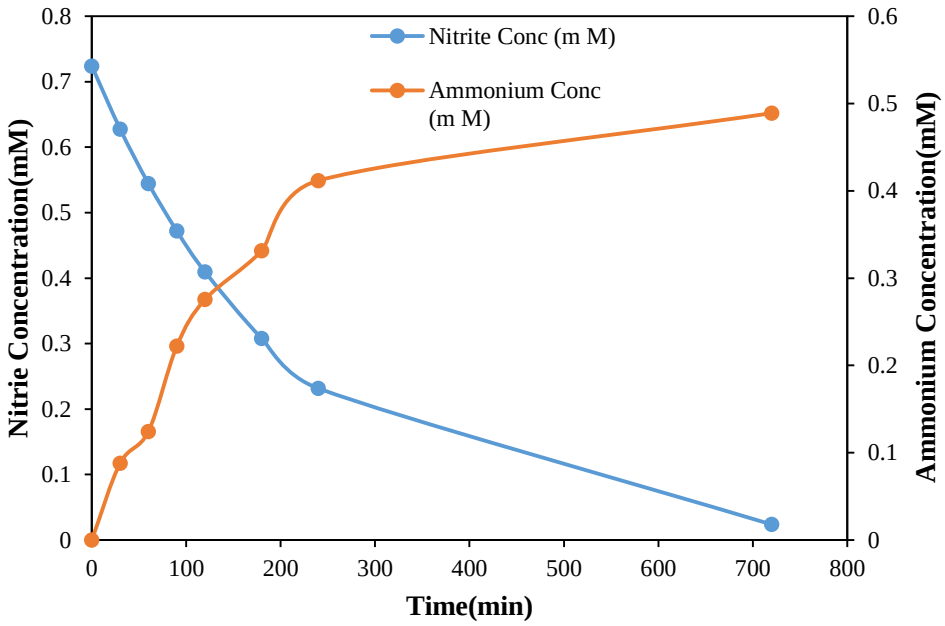


Fig 4.2.2.b Concentration profile for nitrite reversible reactions using MIL-125

From this, we get, $k_1 = 0.003621\ min^{-`1}$ and $k_2 = 0.007504\ min^{-`1}$

Hence, for MIL-125

As, $k_{overall} = k_1 + k_2 + k_3$

$k_3 = k_{overall} - (k_1 + k_2) = 0.02814\ min^{-`1}$

Using this nitrogen and its gaseous oxides content released can be determined. Similar experiments were carried out on conventional photo catalysts. Thus photo degradation efficiency can be represented as MIL-125 > ZnO > TiO_2.

A photo catalyst can reduce nitrite when its electrons are excited to a free state in the conduction band. Once freed, these conduction band electrons can be transferred to nitrite ions adsorbed to the

photo catalyst surface. Concurrently, the excitation of the electron creates a hole in the valence band of the photo catalyst (i.e., electron/hole pair). To maintain electro neutrality the hole must be filled with an electron either through the oxidation of compounds (i.e., electron donor) or from recombination of the electron/hole pair. From the above kinetic parameters it can be inferred that further fine tuning of MIL-125 with various dopants may lead to improved degradation as a way to decrease the recombination rate was to add a metal co-catalyst to the surface of the photocatalyst. The metal can act as an electron trap or sink for conduction band electrons, thus increasing the time available for the hole to be filled and the electrons to complete the interfacial transfer. Successful doping Fe in MIL-125 was carried out, but the resulting product showed lesser photocatalytic activity as shown in Fig 4.2.1.f.

V. CONCLUSIONS AND FUTURE SCOPE

In this work, synthesis and optimization of MIL-125 was successfully carried out on three parameters viz. stirring time, synthesis temperature and synthesis time and using microwave heating. It was found that the microwave synthesis for a reaction time of 40 min and at a temperature of 120 °C was found to match the result reported in the literature for solvo-thermal synthesis of MIL-125. Detailed characterizations were carried out using various techniques like SEM, PXRD, TGA, BET surface area analysis, FTIR and UV reflectance study. A detailed aqueous phase stability study followed which showed its stability under various pH conditions. At present microwave heating seems promising way to achieve short reaction times and fine small crystalline sizes. The specific surface area of approx. 371 m^2/g showed the porous nature of the synthesized samples whereas the corresponding band gap energy value was found to be 3.18 eV. A study on photocatalytic effect by photodegradation of MB dye in MIL-125 has been successfully observed and hence it is photocatalytic in nature and can be used for degradation. Standard curves for waste water substrates such as ammoniacal solution and nitrite solution was prepared and the results followed Beer Lambert's law. Ammonia degradation study was carried out using MIL-125 and the results were found to be consistent. The final degradation of ammonia was found to be approx. 70% and the experimental data were best with pseudo first order kinetic model where the rate constant was found to be 0.03189 min^{-1}.

Additionally, two more variants of MIL-125 were synthesized viz. Fe doped and MIL-125 Solvothermal. Both the products were found to be porous with an experimental measured surface areas of 246 m^2/g and 240 m^2/g, respectively. The corresponding band gap energy were found to be 3.4 eV and 3.2 eV. These preliminary evaluation shows the potential of both the samples and further investigation are necessary to find there effectiveness.

Optimization of degradation of ammonia with MIL-125 based on product distribution is required for adequate scale up of the process for development of commercial products such as catalysts for nitrification and sensors for detection of ammonia. Ti based MOF (MIL-125) can be considered as promising material for adsorption removal and photo degradation of dye pollutant in wastewater

treatment also. Doping of MIL-125 with various d transitional metals to improve degradation of ammonia and reduce the formation of nitrites.

Ti based MOF (MIL-125) can be considered as promising material for adsorption removal and photo degradation of dye pollutant in wastewater treatment also.

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APPENDIX-I

Standard graphs and other profiles:

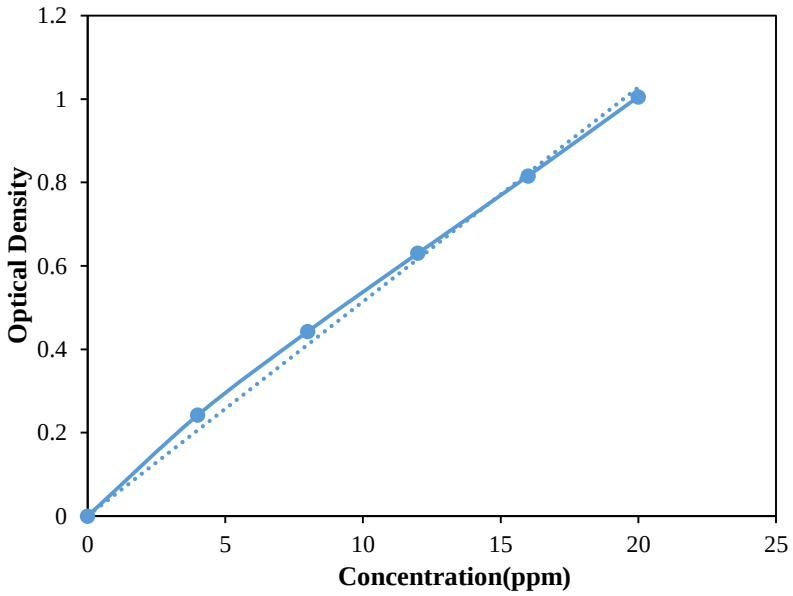

Fig I.a: Standardisation plot for ammonia determination using Nessler Reagent

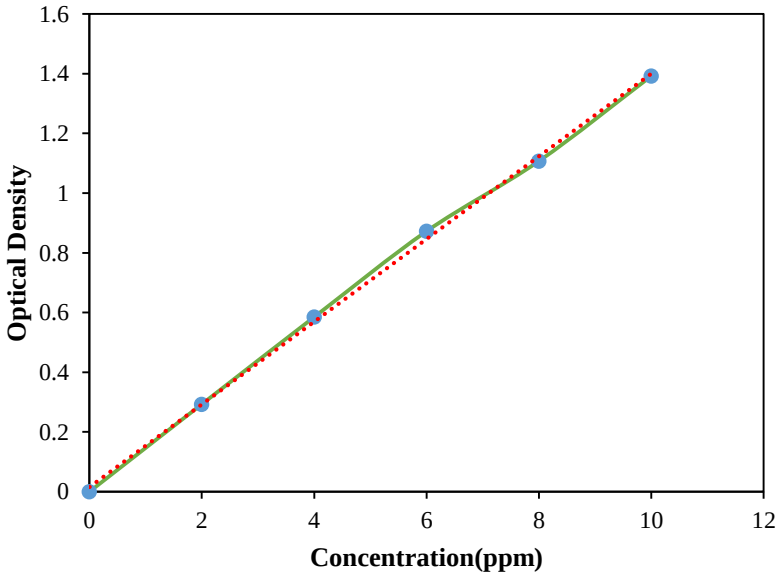

Fig I.a: Standardisation plot for nitrite determination using buffer color reagent

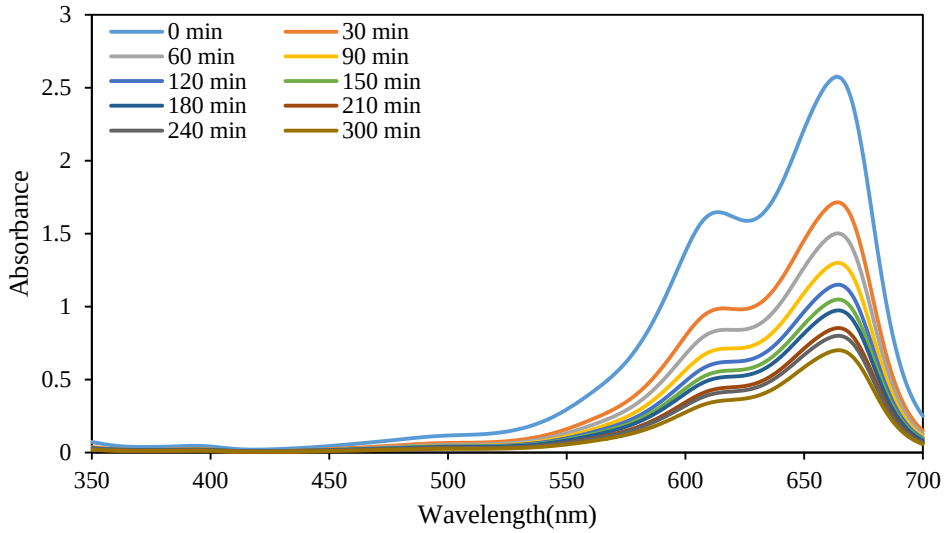

Fig I.b UV Absorbance profile for adsorption of 40 ppm MB solution

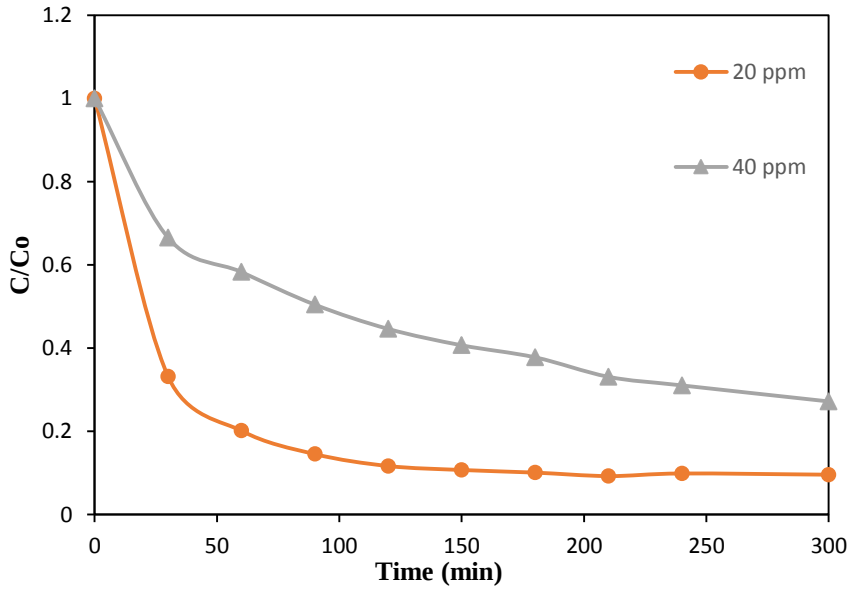

Fig I.c Concentration profile for adsorption of 20 ppm and 40 ppm MB solution